Polymer Science U.S.S.R. Vol. 31, No. 5, pp. 1054–1060, 1989
Printed in Poland

0032-3950/89 $10.00+.00

MAXWELL EFFECT IN POLYMER SOLUTIONS FOR HIGH VELOCITY GRADIENTS*

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(*Received* 3 *September* 1987)

Binomial asymptotics of the angle of orientation and birefringence (b.r.) in solutions of rigid rod-shaped polymeric macromolecules has been found at high velocity gradients. The conditions of applicability of the asymptotic formulae obtained and and the possibility of using them for determining the size of the macromolecules have been established. The use of the results to determine the size of the collagen molecule is demonstrated. The result well agrees with those given in the literature.

THE Maxwell effect – b.r. in solution resulting from the orientation of anisotropic particles (macromolecules) in lamimar flow – is one of the main means of studying the structure of polymeric macromolecules. To determine from the experimentally measured values of the angle of orientation φ_m and b.r. Δn the parameters characterizing the shape and size, mobility and optical properties of the macromolecules it is necessary to have analytical expressions relating φ_m and Δn to these parameters. For low velocity gradients g ($g/2D_r \equiv \sigma \ll 1$, where Dr is the coefficient of rotatory diffusion), the authors of references [1–4] refer to the binomial asymptotics of φ_m and Δn for solutions of rigid macromolecules with the form of an ellipsoid of rotation. The formulae obtained are applicable for $\sigma \lesssim 0{\cdot}7$. However, in the literature [1, 5] emphasis has been repeatedly laid on the need to study φ_m and Δn in the opposite limiting case of high velocity gradients ($\sigma \gg 1$), since for large shear stresses the possible polydispersity of the particles will have a lesser effect on the results of measurement. In reference [6] it is shown that on fulfilment of the condition

$$\sigma(1+b)^2 \gg 1 \tag{1}$$

($b=(1-p^2)(1+p^2)^{-1}$, $p=a_1/a_2$, where a_1, a_2 are the axes of the ellipsoid, $a_1>a_2$), φ_m and Δn break down into asymptotic series for negative degrees of σ and a mononomial asymptotics of φ_m and binomial asymptotics of Δn are found (formulae (12), (3) and (14) in reference [6]). However, for heavily drawn out ellipsoids condition (1) is fulfilled only for transcritical values of the gradient g when the condition of laminarity of flow is violated and in the important limiting case of rod-shaped particles ($p=\infty$ and $b=-1$) to which belong many protein molecules, it is not fulfilled however large the velocity gradients. Thus, the results of reference [6] apply only for solutions with not very extended particles. For solutions of heavily extended particles it is na-

* Vysokomol. soyed. A31: No. 5, 960–965, 1989.